

JAPANESE

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CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS EXAMPLE CORRECTION OR AMENDMENT

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to the pipe for fuel or tank excellent in the stress crack-proof nature and gasoline gas barrier nature to gasoline, especially oxygenated gasoline which has an EVOH resin composition (C) layer.

[0002]

[Description of the Prior Art]The plastic is expected in many fields as a raw material of the container for saving hydrocarbon, for example, gasoline, or the pipe for transporting, and an automotive fuel tank, a fuel pipe, etc. are raised as an example. As a plastic, polyethylene (especially super-high-density polyethylene) is expected in respect of economical efficiency, molding workability, a mechanical strength, etc. However, as for the fuel tank made from polyethylene, having the fault that the gas or fluid of gasoline saved disperses easily in the atmosphere through the wall of polyethylene of a container is known. in order [then,] to cancel this fault -- the container made from polyethylene -- halogen gas (fluoride.) Sulfur trioxide (SO₃), such as chlorine and bromine, etc. are blown into a container, the way the method of halogenating or sulfonating a container internal surface multilayers polyamide resin and polyethylene resin again is devised, and it is put in practical use partly. In recent years also in the polyethylene container processed by the method

as stated above However, for the economy in consumption of gasoline, highly-efficient-izing, and an earth environment improvement, The low alcohols of the boiling points, such as methyl alcohol and ethyl alcohol, Or the oxygenated gasoline which blended ether, such as methyl-t-butyl ether (MTBE), To moisture mixing gasoline and moisture mixing oxygenated gasoline unavoidable in practice at the time of fuel tank use, it has the fault that transmission quantity increases, and an improvement of faults, such as this, is desired.

[0003]Then, the permeability of gasoline and oxygenated gasoline as a very small (barrier property is good) raw material as further corrective strategy, Attentions have gathered for the ethylene-vinylalcohol copolymer (this is called "EVOH" for short below), and the multilayered container which laminated EVOH and polyethylene, or the multilayered pipe which laminated EVOH and polyamide is made as an experiment. To JP,50-103528,A. In the blow molded container or tube shape container which consists of inside-and-outside two-layer, one layer is formed with polyolefine, The blow molded container or tube shape container currently formed with the resin composition which consists of three ingredients of the ethylenic copolymer (Du Pont Surlyn) which the layer of another side makes EVOH a subject and contains a metal ion in this, and nylon has the small transmittance of gasoline, and excelling in oil resistance is introduced.

[0004]As a result, although multilayered constitution objects, such as this, have the good barrier property of gasoline and oxygenated gasoline and a positive examination was made aiming at utilization, it became clear that there was an unexpected big problem. Namely, in the fuel tank of 3 sorts of super-high-density polyethylene (UHDPE) / adhesive resin (Ad)/EVOH/Ad/UHDPE five-layer multilayered constitution for example, If long term storage of the various gasoline is filled up with and carried out, probably because a minute crack will arise on some tanks, gasoline barrier nature may get worse rapidly. As a result of investigating a cause variously, in this multilayered constitution container At the time of gasoline restoration. It became clear that stress with them starts and that EVOH tends to produce a stress crack with oxygenated gasoline and moisture mixing oxygenated gasoline. [the gasoline swelling (rate of a dimensional change) of UHDPE and Ad, large it of EVOH, and] [unusual to difference EVOH] So, development of EVOH excellent in the stress crack-proof nature to gasoline, especially oxygenated gasoline and gasoline barrier nature is one of the important technical problems.

[0005]

[Problem(s) to be Solved by the Invention]This invention provides the pipe for fuel or tank which has the stress crack-proof nature to gasoline, especially oxygenated gasoline, and the gasoline barrier nature using the EVOH resin composition (C) excellent in gasoline barrier nature.

[0006]

[Means for Solving the Problem]The above-mentioned purpose receives ethylene content% of 10-70 mol of EVOH(A)100 weight section, By providing a pipe for fuel or a tank which has further at least a constituent (C) layer which blended at least one sort of thermoplastics (B) 1 chosen

from polyamide, polyolefine, and polyester - 50 weight sections, It is attained by providing a pipe for fuel or a tank which consists of a multilayer-structure object which laminated said constituent (C) layer and a thermoplastic resin layer (D) via an adhesive resin layer (E). This invention persons used a film which blended various thermoplastics etc. to EVOH, and carried out evaluation of stress crack nature to gasoline under 10% ***** distortion conditions, and gasoline barrier nature. As a result, when said thermoplastics (B) was blended with EVOH (A), it found out that a stress crack improved, i.e., a stress crack to gasoline under 10% ***** distortion conditions does not arise.

[0007]In this invention, as thermoplastics (B), (1) Polyamide system resin, such as aliphatic polyamide, amorphous polyamide, and meta-xylylene content polyamide, (2) polyethylene; -- polypropylene; -- ethylene, propylene, and vinyl acetate. A copolymer with vinyl monomers, such as acrylic ester, methacrylic acid ester, acrylic acid, and methacrylic acid; These and an acid anhydride, A vinylsilane system compound or an epoxy group containing compound Copolymerization, or polyolefine; ethylene content % of 50-95 mol which carried out graft polymerization, Polyolefine, (3) aliphatic series, and aromatic polyester, such as an ethylene-vinylacetate copolymer saponification thing of not less than 50% of a saponification degree, are raised.

[0008]Especially when blending polyamide of (1) in this, as compared with a case where polyolefine of (2) is blended, it excels in respect of gasoline barrier nature. As compared with a case where polyamide of (1) is blended when blending polyolefine of (2), the thermal stability of a constituent (C) with EVOH (A) is good, Aggravation of gel and stress crack nature by generating of BUTSU can be prevented also by prolonged operation of a making machine at the time of fabricating operations, such as a film.

[0009]in this invention, EVOH (A) is an ethylene-vinyl ester copolymer saponification thing -- an ethylene content -- respectively -- 10 - 80-mol % -- suitable -- 20 - 70-mol% of the range -- a saponification degree is suitably chosen from not less than 85% not less than 80%. Melt molding nature has a bad ethylene content less than [20 mol %], and, on the other hand, gas barrier nature runs short at more than 80 mol %. In a saponification degree, in less than 80%, gas barrier nature and thermal stability worsen. In this invention, although vinyl acetate is raised as a typical thing as vinyl ester used at the time of EVOH manufacture, other fatty acid vinyl ester (vinyl propionate, vinyl pivalate, etc.) can also be used.

[0010]Also when it contains 0.0002-0.2 mol of vinyl silane compound % as a copolymerization ingredient in EVOH, the compatibility of the melt viscosity of a substrate and this EVOH is improved, Dispersibility is improved on the occasion of a blend of EVOH(s) manufacture of a homogeneous co-extrusion multilayer film is not only possible, but, and it is effective in respect of an improvement of a moldability etc.

[0011]Here, as a vinylsilane system compound, vinyltrimetoxysilane, vinyltriethoxysilane, BINIRUTORI (beta-methoxy-ethoxy) Silang, and gamma-metacryloxy propyl methoxysilane are mentioned, for example.

Especially, vinyltrimetoxysilane and vinyltriethoxysilane are used suitably.

[0012]The purpose of this invention in the range which is not checked Other comonomers, for example, propylene, Butylene, unsaturated carboxylic acid, or its ester {(meta) acrylic acid, (Meta) Copolymerization of acrylic ester methyl, ethyl}, etc. and the vinyl pyrrolidone (N-vinyl pyrrolidone etc.) can also be carried out, and a thermostabilizer, an ultraviolet ray absorbent, an antioxidant, colorant, a filler, and a boron system compound can also be blended further. As gel occurrence prevention, a moldability improvement, and crack preventive measures, especially A hydrotalcite system compound, It is preferred to add a kind of a hindered phenol system, a hindered amine system thermostabilizer, metal salt (for example, calcium stearate, calcium stearate magnesium, etc.) of high-class aliphatic carboxylic acid, or a boron system compound or two sorts or more 0.01 to 1% of the weight.

[0013]A suitable melt index (MI) (190 **) of EVOH used for this invention The melting point value; measured under 2160g load, however a thing near 190 ** or over 190 ** Under 2160g load, Values which measured at two or more temperature more than the melting point, and plotted a horizontal axis and a melt index for a reciprocal of the absolute temperature as a vertical axis with a semilogarithmic graph and for which 190 ** was extrapolated and asked are 0.5-20g/10min. at 0.1-50g/10min., and optimum.

[0014]As aliphatic polyamide of polyamide (B), 6 nylon, 6 and 6 nylon, 6/66 nylon, 6 and 9 nylon, 6 and 12 nylon, 12 nylon, 11 nylon, 6 and 4 nylon, and these elastomers are raised. It is especially preferred that a mole ratio (CH_2 group / NHCO basis = C/N) of CH_2 group in polyamide and a NHCO basis is in the range of 5-12. In the case of $\text{C/N} < 5$, thermal stability with EVOH is bad and it is easy to generate gel etc., and by $\text{C/N} > 12$, compatibility with EVOH is bad and mechanical strengths (tension tenacity and elongation, impact strength, etc.) fall.

[0015]Mixed xylylene diamine which contains meta-xylylene diamine and 80% or less of PARAKI silylenediamine of the whole quantity as meta-xylylene content polyamide, alpha whose carbon number is 6-10 pieces, and a constitutional unit generated from omega-aliphatic dicarboxylic acid -- the inside of a chain -- at least 70-mol % -- a contained polymer is raised.

[0016]As an example of these polymers, poly METAKISHIRI range adipamide, polymetaxylylene SEBAKAMIDO, A homopolymer, and the meta-xylylene / PARAKI silylene adipamide copolymers, such as polymetaxylylene SUPERAMIDO, A copolymer [like / meta-xylylene / PARAKI silylene AZERAMIDO copolymer], And aliphatic diamine like an ingredient of these homopolymers or a copolymer, and hexamethylenediamine, Alicyclic diamine like a piperazine, aliphatic diamine like Paller bis-(2-aminoethyl) benzene, A copolymer etc. which carried out copolymerization of aromatic aminocarboxylic acid like aromatic dicarboxylic acid like terephthalic acid, lactam like epsilon caprolactam, omega-aminocarboxylic acid like gamma-aminoheptanoic

acid, and ****- aminomethyl benzoic acid, etc. are mentioned. In the above-mentioned copolymer, PARAKI silylenediamine is 80% or less to all the xylylene diamine, and is 75% or less suitably. moreover -- setting in a chain a constitutional unit generated from xylylene diamine and aliphatic dicarboxylic acid -- at least -- more than 70 mol % -- it is more than 75 mol % suitably.

[0017]Polymers, such as polyamide described above to these polymer, for example, a spray for preventing static electricity, lubricant, a blocking-proof agent, stabilizer, a color, paints, etc. may be contained. and relative viscosity {96% sulfuric acid solution (1g/100 ml) and 25 **} of this meta-xylylene group content polyamide resin is 1.0 - 5 dl/g, and further 1.5 - 4 dl/g -- **** -- better -- **.

[0018]In DSC measurement, amorphous polyamide does not have an endothermic crystal melting peak on parenchyma, and is mainly a polycondensation body of aliphatic diamine and aromatic dicarboxylic acid. As aliphatic diamine, for example Hexamethylenediamine, 2,2,4-trimethyl hexamethylenediamine, 2,4,4-trimethyl hexamethylenediamine, 2-methylpentanemethylenediamine, Bis-(4-aminoethyl)-methane, 2,2-bis-(4-aminoethyl)-isopropylidene, 1,4 - (1,3)- Diaminocyclohexane, 1,5-diaminopentane, 1,4-diaminobutane, 1,3-diaminopropane, 2-ethyldiaminobutane, etc. are mentioned. A kind or more than it can be simultaneously used for these diamine. Especially, hexamethylenediamine, 2-methylpentanemethylenediamine, 1,5-diaminopentane, 1,4-diaminobutane and 1, and 3-diaminopropane is used suitably.

[0019]As aromatic dicarboxylic acid, isophthalic acid, terephthalic acid, alkylation isophthalic acid, alkylation terephthalic acid, naphthalene dicarboxylic acid, diphenyl ether dicarboxylic acid, etc. are mentioned, for example. A kind or more than it can be simultaneously used for these dicarboxylic acid. Especially, isophthalic acid, terephthalic acid, naphthalene dicarboxylic acid, diphenyl ether dicarboxylic acid, etc. are preferred in respect of thermoforming nature, transparency, gas barrier nature, etc.

[0020]An example as amorphous polyamide And a polycondensation body of hexamethylenediamine and isophthalic acid, A polycondensation body of a polycondensation body of hexamethylenediamine isophthalic acid / terephthalic acid, 2,2,4-trimethyl hexamethylenediamine, and 2,4,4-trimethylhexamethylene diamine terephthalic acid, etc. are mentioned. A polycondensation body of 60 / 40 - 95/5, and the hexamethylenediamine isophthalic acid / terephthalic acid that is in the range of 65 / 35 - 90/10 further is especially preferred for a mole ratio of isophthalic acid/ terephthalic acid.

[0021]As polyolefin system resin (B), polyethylene; polypropylene; ethylene and propylene, Vinyl acetate, acrylic ester, methacrylic acid ester, acrylic acid, To a copolymer with methacrylic acid etc., and said polyolefine, unsaturated carboxylic acid, They are copolymerization or denaturation polyolefin system resin which carries out graft polymerization about the acid anhydride, a vinylsilane system compound, or an epoxy group containing compound, An acid anhydride,

a vinylsilane system compound effective in compatibility with EVOH (A), and a dispersibility improvement, Or copolymerization or denaturation polyolefin system resin which carries out graft polymerization is preferred in an epoxy group containing compound, and an acid anhydride or an epoxy group content system is especially more preferred for high density polyethylene and ethylene propylene rubber as resin again.

[0022]As other polyolefin system resin (B), an ethylene-vinylacetate copolymer saponification thing of not less than 50% of a saponification degree is mentioned the ethylene content 40 - 95-mol%. When ethylene content of this ethylene-vinylacetate copolymer saponification thing is 40% or less, an improvement effect of stress crack-proof nature is not enough, and on the other hand at not less than 95%, a fall of a mechanical strength and gasoline barrier nature due to aggravation of compatibility with EVOH get worse. It is 44-90-mol % desirably suitably that ethylene content is low as a general tendency. About a saponification degree, thermal stability is bad at 50% or less, and it is not desirable from a field of compatibility. It is not less than 60% desirably suitably that a saponification degree is low as a general tendency. an ethylene content of EVOH (A) -- at least 5-mol % and 10 more mol % -- a large thing is desirable.

[0023]Aliphatic polyester and aromatic polyester are raised as polyester (B), To aliphatic polyester, ethylene glycol, propylene glycol, Polyester of aliphatic series diol, such as pentamethylene glycol and hexamethylene glycol, or alicycle fellows diol like cyclohexa methyleneglycol, and aliphatic dicarboxylic acid, such as adipic acid and sebacic acid, etc. can be used. To aromatic polyester, said aliphatic series diol or alicycle fellows diol, and isophthalic acid, It is polyester with aromatic dicarboxylic acid, such as terephthalic acid, alkylation isophthalic acid, alkylation terephthalic acid, naphthalene dicarboxylic acid, and diphenyl ether carboxylic acid.

[0024]Loadings of thermoplastics (B) are 5 - 40 weight section suitably one to 50 weight section to EVOH(A)100 weight section. As for an improvement effect of stress crack-proof nature, less than one weight section is not enough as loadings. On the other hand, if 50 weight sections are surpassed, gasoline barrier nature is not enough.

[0025]When blending polyamide of (1) in the above-mentioned thermoplastics (B), as compared with a case where polyolefine of (3) is blended, it excels in respect of gasoline barrier nature. As compared with a case where polyamide of (1) is blended when blending polyolefine of (3), the thermal stability of a constituent (C) with EVOH (A) is good, Aggravation of gel and stress crack nature by generating of BUTSU can be prevented also by prolonged operation of a making machine at the time of fabricating operations, such as a film.

[0026]In this invention, it is preferred to blend a hydrophobic plasticizer (F) of (A) and/or (B) with a constituent which consists of the above (A) and (B) in many cases. Especially when using polyolefine as (B), it is preferred to blend a hydrophobic plasticizer (F).

[0027]What satisfies the following formula as a hydrophobic plasticizer

here is more preferred.

6.5 \geq 19-CH(A) \times 0.1-SP (F) \geq 1.5 (i)

-1 \leq SP(E)-SP (B) \leq 3.5 (ii)

[, however CH (A) show average ethylene content (mol %) of EVOH (A), SP (F) shows a solubility parameter (formula of Fedors) of a hydrophobic plasticizer (F), and SP (B) shows a soluble parameter (formula of Fedors) of polyolefin system resin (B).]

[0028]Although a cause of an unexpected improvement effect manifestation by hydrophobic plasticizer (F) addition is not certain, stress crack-proof nature by hydrophobic plasticizer (F) addition. an addition of polyolefin system resin (B) is greatly reducible -- that is, By a soluble (parameter) relation, the EVOH resin (A) side slippage is distributed with the priority to polyolefin system resin (B), and a hydrophobic plasticizer (F) is presumed to have been able to measure an improvement of stress crack-proof nature by plasticization of polyolefin resin (B).

[0029]As a hydrophobic plasticizer (F), aromatic ester, aliphatic series ester, phosphoric ester, those epoxy compounds, etc. are mentioned.

[0030]As aromatic ester, dibutyl phthalate, dioctyl phthalate, Diheptylphthalate, JI 2 ethylhexyl lid TETO, dicyclohexyl phthalate, Butyl lauryl phthalate, diisooctyl phthalate, butyl coconut alkyl phthalate, Di-tridecyl phthalate, dilauryl phthalate, di-isodecyl phthalate, Butylbenzyl phthalate, octyl capryl lactam phthalate, dimethyl glycol phthalate, Ethylphthalyl ethylene glycolate, methylphthalyl ethylene glycolate, Butylphthalyl butylene glycolate, dinonyl phthalate, diheptylphthalate, Octyldecyl phthalate, di-tridecyl phthalate, butylbenzyl phthalate, Dicaprylphthalate, JI 355 trimethylhexyl phthalate, isooctyl isodecyl phthalate, dimethoxyethyl phthalate, dibutoxydiethyl phthalate, bis(diethylene glycol monomethyl ether) phthalate, etc. are mentioned.

[0031]As aliphatic series ester, a polypropylene horse mackerel peat, di-isodecyl adipate, A JI 2 methylhexyl horse mackerel peat, a JIKAPURIRU horse mackerel peat, a diisooctyl horse mackerel peat, An octyldecyl horse mackerel peat, isooctyl isodecyl AJIPETO, dibutylfumarate, There are dioctyl fumarate, triethyl citrate, acetyl triethyl citrate, tributyl citrate, acetyl tributyl citrate, ASECHIRUTORI 2 ethylhexyl citrate, etc.

[0032]As phosphoric ester, TORIKURE sill phosphate, phenyl JIKURE sill phosphate, Xylenyl JIKURE sill phosphate, KURESHIRU dixylenyl phosphate, There are triphenyl phosphate, tributyl phosphate, TORIKURORU ethyl phosphate, trioctylphosphate, triethyl phosphate, allyl alkyl phosphate, diphenyl MONOORUSO xenyl phosphate, etc.

[0033]As epoxy compound, epoxy monoester, butylepoxy stearate, There are octylepoxy stearate, epoxy butyl oleate, epoxidation butyl oleate, epoxidation soybean oil, epoxidation linseed oil, epoxidation alkyl oil, epoxidation alkyl oil alcohol ester, etc. Epoxidation soybean oil, epoxidation linseed oil, a JINECHIRU hexyl horse mackerel peat, a diisooctyl horse mackerel peat, dibutyl phthalate, diethyl phthalate, JI 2 ethylhexyl phthalate, methylphthalyl ethylene glycolate, etc. are used

suitably especially.

[0034]190 ** of a constituent which blended a hydrophobic plasticizer (F) with a constituent of EVOH (A) and thermoplastics (B), or this, and MI under 2160g load -- 0.1-50g/10min. -- they are 0.3-30g/10min. suitably.

[0035]About the above (A) and (B), and a method of blending (C) to this further, Although not limited in particular, there are a method of carrying out dry BUNREDO of EVOH and this thermoplastics, and using as it is, or pelletizing and drying with the Bambari mixer, a monopodium, or a 2 axis screw extruder more suitably, etc. When a blend is uneven and there are gel, generating of BUTSU, and mixing at the time of blend pelletizing operation, a possibility that a crack will occur is large.

Therefore, it is desirable to use a high extrusion machine of a degree of mulling at the time of blend pelletizing operation, to carry out N₂ seal of the hopper mouth, and to carry out extrusion at low temperature. When blending and pelletizing, it is free to use other additive agents (a plasticizer, a thermostabilizer, an ultraviolet ray absorbent, an antioxidant, colorant, a filler, a boron system compound, other resin, etc.) in the range from which the purpose of this invention is not prevented. Especially a thing for which a kind of metal salt (for example, calcium stearate etc.) of a hydrotalcite system compound, a hindered phenol system, a hindered amine system thermostabilizer, and high-class aliphatic carboxylic acid or two sorts or more are added 0.01 to 1% of the weight as a measure against gel occurrence prevention is preferred.

[0036]Although a pipe for fuel or a tank of this invention has at least one layer of layers of a constituent (C) which blended (F) with the above, (A) and (B), or this, what laminated other thermoplastics (D) layers is suitable for it in a constituent (C) layer. 5-250 micro of thickness of a constituent (C) layer which gives gas barrier property and gasoline barrier nature is usually chosen from 10-the range of 100micro. On the other hand, although arbitrary things are adopted and thermoplastics (D) used for a inner layer and/or an outer layer does not have restriction in particular, a multilayer-structure object of gasoline barrier nature outstanding by considering points, such as moisture permeability, heat resistance, and heat-sealing nature, depending on the purpose can be acquired. As thermoplastics (D), polypropylene, polyolefin system resin, Polyamide system resin, polyester system resin, polystyrene system resin, polyvinyl chloride system resin, Acrylic resin, polyvinylidene chloride system resin, polyacetal system resin, Polycarbonate system resin, polyurethane resin, and polypropylene that carried out exposure bridge construction, Polyethylene, an ethylene-vinylacetate copolymer, an ethylene-vinyl acetate system copolymer saponification thing, An ethylene-acrylic acid series copolymer, an ethylene-methacrylic acid series copolymer, an ethylene-acrylic ester system copolymer, an ethylene-methacrylic-acid-ester system copolymer, etc. are mentioned, and high density polyethylene, polypropylene, and polyamide are used suitably especially. To resin used for both outer layers, additives which were mentioned above, such as an antioxidant, colorant, and a bulking

agent, may be added.

[0037]When laminating a constituent (C) and this thermoplastics (D) in this invention, in order to raise stress crack nature, it is preferred to use adhesive resin (E). As adhesive resin, if a constituent (C) layer and this thermoplastics (D) layer are pasted up firmly, Although not limited in particular, unsaturated carboxylic acid or its anhydrides (maleic anhydride etc.) Polypropylene, olefin system polymers, such as polyethylene, or ethylene, and a monomer (vinyl acetate.) that can carry out copolymerization of this What carried out the graft to a copolymer [for example, ethylene-vinylacetate copolymer and ethylene-(meta) acrylic ester (methyl ester or ethyl ester) copolymer] with acrylic ester etc. is used suitably.

[0038]As a method of acquiring a multilayer-structure object, a constituent (C) and thermoplastics (D) via adhesive resin (E) Extrusion laminating method, A method of acquiring film state, a sheet shaped, pipe shape, a tank (** bottle)-like structure, especially a multilayer-structure object by the dry laminate method, the co-extrusion laminating method, coextrusion process, coinjection-molding method, co-extrusion inflation molding method, the solution coat method, etc. is raised. reheating a structure in the range below the melting point of EVOH, when obtaining this structure -- the roll extending method, the pantographic extending method or the inflation extending method, the blow extending method, etc. -- one axis -- or biaxial stretching can be carried out. This multilayer-structure object is irradiated with radiation, an electron beam, ultraviolet rays, etc., at the time of constructing a bridge in a constituent (C) layer and a thermoplastics (D) layer, or extrusion molding, a chemicals cross linking agent can be added and chemicals bridge construction can also be carried out.

[0039]When a moldability, cost, etc. are taken into consideration also about thickness composition of a multilayer-structure object, about 2 to 20% of a thickness ratio of an EVOH constituent layer to total thickness is suitable. Physical relationship with a thermoplastics (D) layer in an interlayer's constituent (C) layer, both outer layers, or a piece outer layer, Influence barrier property and stress crack nature greatly, and A tank or the inside of a pipe, Namely, stress crack nature improves and barrier property may get worse depending on a brand of gasoline, so that a constituent (C) layer is located inside, when a layer which touches a inner layer and the open air with a layer in contact with fuel, such as gasoline, is made into an outer layer. Stress crack nature may have so good the gasoline barrier nature of what worsening that a constituent (C) layer is located in the outer layer side contrary to this. Therefore, it is desirable for a constituent (C) layer to take composition which is not located in the center of an outer layer and a inner layer generally. As composition of a multilayer-structure object, the EVOH constituent (C) layer / adhesive resin (E) layer / thermoplastics (D) layer, the thermoplastics (D) layer / adhesive resin (E) layer / EVOH constituent (C) layer, the /adhesive resin (E) layer / EVOH constituent (C) layer / adhesive resin (E) layer / thermoplastics (D) layer thermoplastics (D) layer, etc. are typical -- a thing is carried out. When providing a

polyolefin resin layer in both outer layers, this resin may differ and it may be the same. Scraps, such as a trim generated at the time of shaping, are blended to a thermoplastic resin layer, or a recovery layer is provided separately and a reuse is carried out in many cases.

[0040]A pipe for a gasoline transfer used for a pipe for gasoline supply, and a car with a pipe for fuel here, Meaning [and] a pipe for petroleum supply, a pipe for a petroleum transfer used for an oilstove, etc., a tank for fuel means a storage tank etc. which are used for a gasoline storage tank, a storage bottle, a gas tank used for a car, a petroleum storage tank, a storage bottle, and an oilstove.

[0041]These pipes or tanks are obtained by the co-extruding method, the co-injecting method, etc. as they were described above, but can obtain a film state thing and a sheet like object, and can also obtain a pipe or a tank using this.

[0042]

[Example]Hereafter, although this invention by an example is explained in more detail, this invention is not limited to this.

Example 1 ethylene-content % and 99.5% of the saponification degree of 27 mol, EVOH(A)100 weight section of MI(190 **, 2160g load)

1.5g/10min., and 6-12 polyamide (A shows to C/N=7 and Table 1.)

GURIRAKKUSU XE3116 40 weight section was put into the 2 axis screw type and the vent type 40phi extrusion machine, and it pelletized by extruding at 200 ** under a nitrogen atmosphere. MI of the obtained resin (C) was 4g/10min. This pellet was supplied to monolayer film molding equipment, a 100-micro film was obtained, and it was immersed in the basis of tensile elongation rate addition, and 40 ** gasoline (commercial regular gasoline) 10% for 3 hours using the JIS dumbbell No. 3, and the crack was not accepted although stress crack nature was evaluated.

[0043]The multilayered container was created using this pellet with a three-sort five-layer co-extrusion multilayer direct blow device. Both the outermost layers the composition of a multilayered container 850 micro each of high-density-polyethylene resin layers (HDPE, high ZEKKUSUHZ8200B made from Mitsui Petrochemistry), 100 micro of adhesive resin layers (AD-1, ADOMANF450A made from Mitsui Petrochemistry) are 100micro of the above-mentioned EVOH constituent (C) layers each in the center of an innermost layer further. Although the obtained container was filled up with gasoline and it was neglected for one year under the conditions of 40 ** and 65%RH, the crack was not observed in a container, and the fall of gasoline barrier nature was not accepted. As an accelerated test, the drum section of this container was cut off, and although it was immersed in the basis of tensile elongation rate addition, and 40 ** gasoline 10% for 3 hours using the JIS dumbbell No. 3 like the above-mentioned film and stress crack nature was evaluated, the crack was not accepted. The gasoline barrier nature of this container was 0.010 g/m² and day.

[0044]The pellet of the EVOH resin composition (C) was obtained by the method indicated in the Example 1 using EVOH(A)100 weight section and amorphous polyamide (B. Ube Industries, Ltd. make 12-

nylon X-21) 40 weight section which were used for example 2 Example 1. Obtain a 100-micro film like Example 1 using this pellet, and using the JIS dumbbell No. 3 The basis of 10% tensile elongation rate addition, Generating of the crack was not accepted, although 40 ** was immersed in Ref-C (mixed gasoline which consists of toluene 50% and isooctane 50%) for 3 hours and the stress crack was evaluated. The multilayered container was created with a three-sort five-layer co-extrusion direct blow device like Example 1 using this pellet. Although the obtained container was filled up with Ref-C mixed gasoline and it was neglected for one year under the conditions of 40 ** and 65%RH, the crack was not observed in a container, and the fall of gasoline barrier nature was not accepted. The accelerated test was done still like Example 1, and the crack was not accepted, although it replaced with the gasoline of Example 1 and the stress crack nature to Ref-1 was evaluated. The gasoline barrier nature of this container was the outstanding thing, and as shown in Table 1, it was 0.0005 g/m² and day.

[0045]The pellet of the EVOH resin composition (C) was obtained by the same method as the method indicated in the Example 1 using EVOH (A)100 weight section and meta-xylylene system polyamide (Mitsubishi Gas Chemical Co., Inc. make MXD-6) 40 weight section which were used for example 3 Example 1. A 100-micro monolayer film was obtained using this pellet, and generating of the crack was not accepted although the stress crack to Ref-C was evaluated like Example 2. The multilayered container was created with a three-sort five-layer co-extrusion direct blow device like Example 1 using this pellet, and the stress crack nature and gasoline barrier nature to Ref-C mixed gasoline were measured like Example 2. It was the multilayered container which was excellent in any character in the result as shown in Table 1.

[0046]The pellet of the EVOH resin composition (C) was obtained by the same method as the method indicated in the Example 1 using EVOH (A)100 weight section used for example 4 Example 1, and ethylene-vinylacetate copolymer saponification thing (inside [of Table 1] D, and statement) 40 with an ethylene content [% and 95% of the saponification degree of 50 mol] weight section. A 100micro film was obtained like Example 1 using this pellet. The multilayered container was manufactured with a three-sort five-layer co-extrusion direct blow device like Example 1 using this pellet. The stress crack nature and gasoline barrier nature to Ref-C mixed gasoline were measured like [this / monolayer film and multilayered container] Example 2. The result was excellent in all, as shown in Table 1.

[0047]As EVOH(A)100 weight section and thermoplastics (B) of example 5 ethylene-content % and 99.5% of the saponification degree of 27 mol, and 1.5g of melt indices (MI190 **, 2160g load) / 10min., Ethylene-vinyl acetate copolymer saponification thing 20 with an ethylene content [% and 95% of the saponification degree of 50 mol] weight section was put into the 1 axis 40phi extrusion machine, and it pelletized by extruding at 200 ** under N₂. MI of the obtained resin (C) was 2.5g/10min. Supply this pellet to monolayer film molding

equipment, obtain a 100-micro film, and using the JIS dumbbell No. 3. The basis of 10% tensile elongation rate addition, The crack was not accepted, although it was immersed in 40 ** and methanol 15% content model gasoline (isooctane + toluene (50vol%)) for 3 hours and stress KURASSU nature was evaluated. It applied to four-sort five-layer co-extrusion multilayered pipe molding equipment using this pellet, and the multilayered pipe was created. Outermost layer 12 polyamide (UBE nylon 30200 by Ube Industries, Ltd.) the composition of a pipe 450 micro, An adhesive resin layer (AD-2 product [made from Mitsui Petrochemistry] ADOMAVF500) Next, 50 micro each, It is the further 6 polyamide (Toray Industries, Inc. make east rare milan CM1046) 100 micro and 150micro of the above-mentioned EVOH constituent (C) layers, and an innermost layer is the 6 polyamide (Toray Industries, Inc. make east rare milan CM1046) 250 micro. Metallic metal fitting is attached to the end of the obtained pipe, and it winds around looped shape at R(radius) = 30 cm, and is gasoline (shown all over [M-15] Table 1.). Although it was filled up with the mixed gasoline of Ref-C85 capacity % and methanol 15 capacity % and was neglected for one year under 40 **-65%RH conditions, aggravation of a crack and gasoline barrier nature was not accepted. So that the drum section of this pipe may be cut into round slices and a tensile elongation rate can be added 10% as an accelerated test, This round slice pipe was extended with the cylindrical jig with a peripheral diameter long [10% of pipe internal diameter boundary-length halfbeak] (10% tensile elongation rate addition), and the crack was not accepted, although it was immersed in 40 ** and M-15 mixed gasoline for 3 hours and stress crack nature was evaluated. The gasoline barrier nature of this pipe was 0.2 g/m² and day. [0048]Instead of the thermoplastics (B) used in example 6 Example 5, ethylene content % of 90 mol, Using the ethylene-vinyl acetate copolymer saponification thing of not less than 90% of a saponification degree, MBE-15 (mixed gasoline of Ref-C 85 capacity % and MTBE 15 capacity %) was used instead of M-15 gasoline, and operation of Example 5 was repeated. The result is shown in Table 1. [0049]The pellet was manufactured for EVOH (A) used for comparative example 1 Example 1 using the 2 axis screw type and vent-type 40 phi extrusion machine, and a 100-micro monolayer film was manufactured for this pellet by the same method as Example 1. The multilayered container was manufactured with a three-sort five-layer co-extrusion direct blow device like Example 1 using this pellet. The result measured like [this / monolayer film and multilayered container] Example 2 about the stress crack nature and gasoline barrier nature to Ref-C mixed gasoline was shown in Table 1.

[0050]

[Table 1]

EVOH組成物(C)				多層構造体の構成						多層構成体の特性			
EVOH(A)		EVOH(B)		最外層	接着層	中間層	EVOH	接着層	最内層	形状	ストレスクラック性	ガスリソバリアー性	
エチレン含有量モル%	酸化度モル%	添加量	銘柄	850μ	100μ	100μ	100μ	100μ	850μ		EVOH	ガソリン	1ヶ月
		重量部									単層	銘柄	1年
実験例 1	27	99.5	A	HDPE	AD-1	—	EVOH	AD-1	HDPE	容器	なし	ガソリン	0.010
2	27	99.5	B	HDPE	AD-1	—	EVOH	AD-1	HDPE	容器	なし	Ref-C	0.005
3	27	99.5	C	HDPE	AD-1	—	EVOH	AD-1	HDPE	容器	なし	Ref-C	0.005
4	27	99.5	D	HDPE	AD-1	—	EVOH	AD-1	HDPE	容器	なし	Ref-C	0.003
5	27	99.5	D	12PA	AD-2	6-PA	EVOH	—	6-PA	パイプ	なし	M-15	0.20
				(450μ)	(50μ)		(150μ)		(250μ)				
6	27	99.5	E	12PA	AD-2	6-PA	EVOH	—	6-PA	パイプ	なし	MBE-15	0.020

比較例 1	27	99.6		0	HDPE	AD-1		EVOH	AD-1	HDPE	容器	あり	あり	Ref-C	0.001	測定不可
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(**) The numerals in Table 1 are as follows.

(1) brand of thermoplastics (B) A EMS polyamide . GURIRAKKUSU XE3116 B Ube Industries, Ltd. make Amorphous polyamide X-21 C Mitsubishi Gas Chemical Co., Inc. make Meta-xylylene system polyamide MXD-6 D ethylene-vinylacetate copolymer saponification thing (ethylene content % of 50 mol)

E * * * * * (** 90-mol %)

(2) A multilayer-structure object. brand of the thermoplastics to constitute HDPE -- product made from Mitsui Petrochemistry High ZEKKUSU HZ8200B 6PA Toray Industries, Inc. make Alamine CM1046 12PA -- Ube Industries, Ltd. make UBE nylon 30200 AD-1 -- product made from Mitsui Petrochemistry . Brand of ADOMA NF450A AD-2 * * * * * VF500 (3) gasoline Gasoline Commercial regular gasoline Ref-C Toluene (50 capacity %) + isooctane (50 capacity %) M-15 Ref-C(85 capacity %)+ methanol (15 capacity %) MBE-15 Ref-C(85 capacity %)+ methylbutyl Tasha RUBUCHIRU Ether (15 capacity %)

[0051]example 7 ethylene-content % and 99.5% of the saponification degree of 27 mol, and a melt index (MI -- 190 **) as EVOH(A)100 weight section and thermoplastics (B) of 1.5g of 2160g load / 10min. -- the GMA (glycidyl methacrylate) denaturation HDPE (high density polyethylene.) SP(B) =8.6 10 weight section and GMS(glycerol monostearate, SP(E) =10.2) 4 weight section were put into the 2 axis screw type and the vent type 40phi extrusion machine, and it pelletized by extruding at 200 ** under N₂ atmosphere. The * * * * * indices (MI) of the obtained resin (C) were 1g/10min. This pellet was supplied to monolayer film molding equipment, a 100-micro film was obtained, and the crack was not accepted, although it was immersed in the basis of tensile elongation rate addition, and 40 ** gasoline (commercial regular gasoline) 10% for 3 hours using the JIS dumbbell No. 3 and stress crack nature was evaluated. It applied to a three-sort five-layer co-extrusion multilayer direct blow device using this pellet, and the multilayered container was created. Both the outermost layer high-density-polyethylene resin layer (high ZEKKUSUHZ8200made from Mitsui Petrochemistry B) is [850micro of adhesive resin layers / 100 micro of / (Mitsui petrochemical ADOMANF450A) of the composition of a sheet] 100micro of the above-mentioned EVOH constituent (C) layers each in the center of an innermost layer further again. Although the obtained container was filled up with gasoline and it was neglected for one year under 40 *-65%RH conditions, aggravation of a crack and gasoline barrier nature was not accepted. As an accelerated test, the drum section of this container was cut off, and although it was immersed in the basis of tensile elongation rate addition, and 40 ** gasoline 10% for 3 hours using the JIS dumbbell No. 3 like the above-mentioned monolayer film and stress crack nature was evaluated, the crack was not accepted. The gasoline barrier nature of this container was 0.020 g/m².day.

[0052]Glycidyl methacrylate denaturation HDPE(high density

polyethylene)10 weight section as thermoplastics (B) to EVOH(A)100 weight section used in example 8 Example 7 A 2 axis screw type, It put into the vent type 40phi extrusion machine, and under a nitrogen atmosphere, it extruded at 200 °C and the pellet was produced. After using this pellet as a 100-micro film by the same method as Example 7, this film was immersed in the basis of tensile elongation rate addition, and 40 °C Ref-C gasoline 10% for 3 hours using the JIS dumbbell No. 3, and stress crack nature was evaluated. The multilayered container was manufactured by the same method as Example 7 using this pellet. The stress crack nature and gasoline barrier nature to Ref-C gasoline are measured about this container, and that result is shown in Table 2.

[0053]The same operation as Example 8 was repeated except having made into 40 weight sections quantity of the thermoplastics (B) used for example 9 Example 8 to EVOH(A)100 weight section. The result is shown in Table 2.

[0054]replacing with the thermoplastics (B) used in example 10 Example 7 -- HDPE (high density polyethylene.) The stress crack nature and gasoline barrier nature of the monolayer film and the multilayered container which were replaced with commercial regular gasoline using SP (B) =8.6, and were manufactured according to Example 7 using Ref-C gasoline were measured. The result is shown in Table 2.

[0055]replacing with the thermoplastics (B) used in example 11 Example 7 -- the maleic anhydride denaturation HDPE (high density polyethylene.) SP(B) =8.6 -- as a hydrophobic plasticizer, diethyl phthalate (DEP, SP(E) =10.5) was used instead of GMS, Ref-C gasoline was further used instead of commercial regular gasoline, and operation of Example 7 was repeated. The result is shown in Table 2.

[0056]Replace with the thermoplastics (B) used in example 12 Example 7, and Si denaturation ethylene propylene rubber (SP (B) =8.4) is used, DEP was used instead of GMS as a hydrophobic plasticizer, it replaced with commercial regular gasoline further, and operation of Example 7 was repeated using MTBE15 gasoline. The result is shown in Table 2.

[0057]It applied to four-sort five-layer co-extrusion multilayered pipe molding equipment using the EVOH constituent (C) used in example 13 Example 1, and the multilayered pipe was created. Outermost layer 12 polyamide (Ube Industries, Ltd. UBE nylon 3020 mu) the composition of a pipe 450 micro, Next, adhesive resin layers are 50 micro each, the further 6 polyamide (Amilan CM1046 by Toray Industries, Inc.) 100 micro, and 150micro of the above-mentioned EVOH constituent (C) layers, and an innermost layer is the 6 polyamide (Amilan CM1046 by Toray Industries, Inc.) 250 micro. Metallic metal fitting was attached to the end of the obtained pipe, and it wound around looped shape at R (radius) = 30 cm, and although it was filled up with gasoline (M-15) and was neglected for one year under 40 °C-65%RH conditions, aggravation of a crack and gasoline barrier nature was not accepted. So that the drum section of this pipe may be cut into round slices and a tensile elongation rate can be added 10% as an accelerated test, The crack was not accepted, although the round slice pipe was extended with the cylindrical jig with a peripheral diameter long [10% of pipe internal diameter

boundary-length halfbeak] (10% tensile elongation rate addition), it was immersed in 40 ** M-15 gasoline for 3 hours and stress crack nature was evaluated. The gasoline barrier nature of this pipe was 0.2 g/m² and day. [0058]It replaced with the hydrophobic plasticizer (C) used in comparative example 2 Example 7, and operation of Example 7 was repeated using glycerin (Gly, SP(E) =16.4) which is a hydrophilic plasticizer. The result is shown in Table 2.

[0059]

[Table 2]

EVOH組成物(C)						多層構造体の構成						多層構成体の特性					
熱可塑性樹脂(B)		熱可塑性樹脂(E)		関係式		最外層	接着層	中間層	EVOH	接着層	最内層	形状	ストレスクラック性		ガリソンバリヤー-性		
銘柄	添加量 重量部	銘柄	添加量 重量部	(i)の 値	(ii)の 値	850μ	100μ	100μ	100μ	100μ	850μ		EVOH 単層	多層	1ヶ月	1年	
(g・20μ/m ² ・day.)																	
A	10	GMS	4	6.1	1.6	HDPE	AD-1	—	EVOH	AD-1	HDPE	容器	なし	なし	ガリソン	0.020	
A	10	—	—	—	—	HDPE	AD-1	—	EVOH	AD-1	HDPE	容器	なし	なし	Ref-C	0.065	
A	40	—	—	—	—	HDPE	AD-1	—	EVOH	AD-1	HDPE	容器	なし	なし	Ref-C	0.068	
D	10	GMS	4	6.1	1.6	HDPE	AD-1	—	EVOH	AD-1	HDPE	容器	なし	なし	Ref-C	0.076	
B	10	DEP	4	5.8	1.6	HDPE	AD-1	—	EVOH	AD-1	HDPE	容器	なし	なし	Ref-C	0.019	
C	10	DEP	4	5.8	2.1	HDPE	AD-1	—	EVOH	AD-1	HDPE	容器	なし	なし	NTBE15	0.018	
A	10	GMS	8	6.1	1.6	12PA	AD-2	6-PA	EVOH	—	6-PA	パイプ	なし	なし	N-15	0.210	
						(450μ)	(50μ)		(150μ)		(250μ)						
A	10	Gly	4	-0.1	7.8	HDPE	AD-1		EVOH	AD-1	HDPE	容器	なし	なし	ガリソン	0.250	

	EVOH(A)		酸化度		モル%		モル%		モル%		モル%	
	エチレン		含有量		モル%		モル%		モル%		モル%	
	実施例 7		27		99.5		27		99.5		27	
	8		27		99.5		27		99.5		27	
	9		27		99.5		27		99.5		27	
	10		27		99.5		27		99.5		27	
	11		27		99.5		27		99.5		27	
	12		27		99.5		27		99.5		27	
	13		27		99.5		27		99.5		27	
	比較例 2		27		99.5		27		99.5		27	

(**) The numerals in Table 2 are as follows.

(1) Brand A of thermoplastics (B) Glycidyl methacrylate denaturation HDPE (high density polyethylene)
B Maleic acid denaturation HDPEC Silicon (Si) denaturation ethylene propylene copolymer D HDPE (high density polyethylene)

(2) Brand GMS of a hydrophobic plasticizer (C) Glycerol monostearate DEP Diethyl phthalate Gly Glycerin (hydrophilic plasticizer)

(3) The brand of the thermoplastics which constitutes a multilayer-structure object (it is the same as (2) of Table 1)

(4) The brand of gasoline (it is the same as (3) of Table 1)

[0060]

[Effect of the Invention]Thus, the obtained pipe for fuel or tank of this invention is excellent in the stress crack-proof nature to gasoline. And gasoline barrier nature is good and gas barrier nature, a smell retaining property, or organic solvent-proof nature is further excellent.

[Translation done.]